for N. F. H. Bright

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

MINES BRANCH

OTTAWA

MINERAL SCIENCES DIVISION

INTERNAL REPORT MS-65-31

SYNTHETIC WODGINITE, TAPIOLITE AND TANTALITE

by

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Physical Chemistry Section

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Paper prepared for presentation to the Mineralogical Association of Canada, Toronto, March 8-10, 1965.

February 22, 1965

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TITLE: Synthetic Wodginite, Tapiolite and Tantalite.

(Date) February 23rd, 1965

Internal

~~Investigation~~ Report No. MS-65-31

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Mineral Sciences Division Report MS-65-31

SYNTHETIC WODGINITE, TAPIOLITE AND TANTALITE

by

A.C. Turnock*

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INTRODUCTION

Wodginite was discovered by E.H. Nickel in pegmatite from Bernic Lake, Manitoba, and further study led to a definition of this mineral. (Nickel, Rowland and McAdam, 1963). It was found to be chemically and structurally related to columbite-tantalite.

Chemically, both wodginite and columbite-tantalite are complex oxides of Fe, Mn, Ta and Nb, plus minor substitutions by Ti and Sn, with cations: anions = 1:2. Columbite-tantalites have the formula $(Mn, Fe)_4(Nb, Ta)_8O_{24}$ or AB_2O_6. Nickel et al found wodginite to be $A_{16}O_{32}$, where A represents chiefly Ta, Sn and Mn. It is demonstrated below that tin is not an essential element for its formation, that it may contain ferric but not ferrous iron, and that it is a solid solution between AB_2O_6 and ABO_4.

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Crystallographically, Nickel and Rowland deduced the structural similarity between wodginite and columbite-tantalite, with the unit cells related by: $a_W \Xi 2/3\, b_C$, $b_W \Xi 2a_C$, and $c_W \Xi c_C$ (subscripts W and C for wodginite and columbite-tantalite, respectively). Wodginite is monoclinic ($\beta = 91° 18'$), columbite-tantalite is orthorhombic, but this involves only a slight distortion without destroying the structural similarity. The structural similarity of columbite and wolframite was noted by Schröcke (1961) and detailed by Laves, Bayer and Panagos (1963). Broch (1929) originally discussed as the wolframite-group some ABO_4 compounds that had similar structures; Laves et al and Roth and Waring (1964) have expanded and formulated this family relationship. The unit cell of columbite may be described as a supercell formed by triple repetition of an orthorhombic wolframite sub-cell along one axis (the a of wolframite in its usual setting with a = 4.78, b = 5.73, c = 4.98), caused by ordering of the cations. The unit cell of wodginite, which must be added to the group, may be described as a supercell of a monoclinic wolframite sub-cell, with double repetition along a and b. The group contains both orthorhombic and monoclinic members, structurally related by a slight distortion. This distortion is well shown in the wolframite series, where the angle β changes from 90° 00′ in $FeWO_4$ to 91° 10′ in $MnWO_4$ (Sasaki, 1959). Roth and Waring referred to the cation-disordered orthorhombic ABO_4 structures as "ixiolite-type".

EXPERIMENTAL PROCEDURE

Crystalline materials were synthesized from reagent grade chemicals, and reacted in a quench furnace under controlled conditions of temperature and partial pressure of oxygen. The total pressure was one atmosphere for all experiments.

Oxidation and reduction reactions between solids and vapour took place. Any changes in the bulk composition, caused by changes in the oxygen content, were determined from weight changes.

At the completion of the heating time, the charge was lowered quickly to the cool end of the furnace, where it cooled to room temperature in the stream of gas entering the furnace, in about half a minute. No reactions were suspected to take place during this cooling period.

The phases were identified by powder X-ray diffraction.

THE SYSTEM $MnTa_2O_6$ - $FeTa_2O_6$

In order to keep the manganese and iron in the bivalent state, as required in this system, the partial pressure of oxygen (f_{O_2}) in the furnace was controlled at a low value, i.e., the univariant f_{O_2} of the iron-wüstite equilibrium by employing the $CO:CO_2$ ratios determined by Darken and Gurry (1945).

It was found that chemical mixtures, viz., $Fe_2O_3 + MnC_2O_4.2H_2O + Ta_2O_5$, or $FeC_2O_4.2H_2O + MnC_2O_4.2H_2O + Ta_2O_5$, reacted quickly when heated at temperatures greater than 1000°C

to produce the more stable complex oxides. At 1200°C, the reactions were completed in two hours. The products were one or both of the following phases: (1) orthorhombic $Mn_{1-x}Fe_xTa_2O_6$, here referred to by its mineral name tantalite, and (2) tetragonal $Fe_{1-y}Mn_yTa_2O_6$, here referred to as tapiolite. Their distribution is shown in Figure 1.

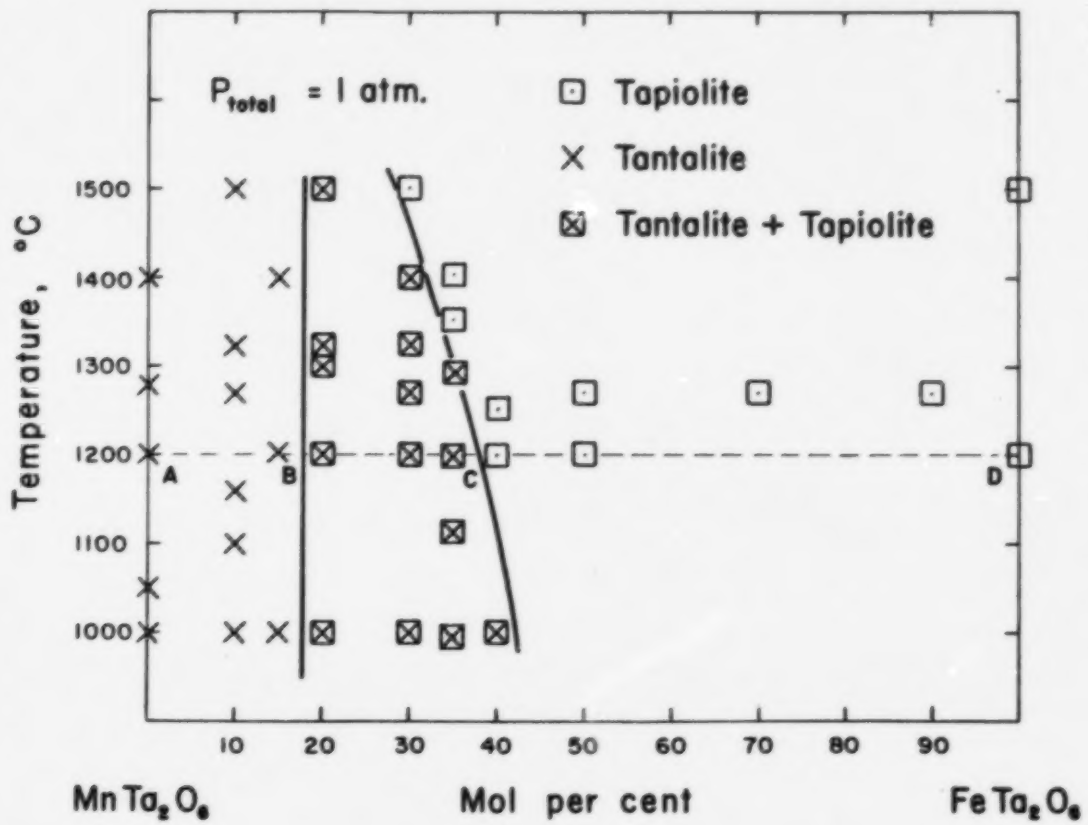

Figure 1. The system $MnTa_2O_6$-$FeTa_2O_6$. The data points present the results of synthesis for various lengths of time, plus reversals of the equilibrium along the tapiolite field boundary.

Tantalite can take up to 18 mol.% $FeTa_2O_6$ into solid solution, and this limit is insensitive to temperature variation. In contrast, the maximum amount of solid solution of tantalite in tapiolite decreases with increasing temperature; at 1200°C, point C in Figure 1, it is 62 mol.% $MnTa_2O_6$.

The MnO content of natural tapiolites, and the FeO content of natural mangano-tantalites, as shown in compilations of analyses (Palache, Berman and Frondel, 1944) are mostly withing the limits of the synthetic ranges from Figure 1. The comparison is not exact, because of the presence of additional components, especially Nb_2O_5, in the natural materials.

THE SYSTEM $MnTa_2O_6$ - $FeTa_2O_6$ - O

The oxidation of tantalites and tapiolites in the system $MnTa_2O_6$-$FeTa_2O_6$ was studied at various partial pressures of oxygen, and the results are shown in Figure 2. The base of this diagram is the 1200° isotherm from Figure 1, and points marked A, B, C and D are at the boundaries of the fields of tantalite and tapiolite.

End-member tantalite, $MnTa_2O_6$, remained stable under the most oxidising condition, which was 1 atm. P_{O_2}. In contrast, the iron-bearing compounds underwent oxidation thus:

$$2\,Fe^{+2}Ta_2O_6 + \tfrac{1}{2}\,O_2 \rightleftharpoons 2\,Fe^{+3}TaO_4 + Ta_2O_5$$

Small amounts of exsolved Ta_2O_5 were found with all the oxidized Fe-bearing products. Tapiolites were partially oxidized at medium partial pressures of oxygen, with $FeTaO_4$ remaining in solid solution by the

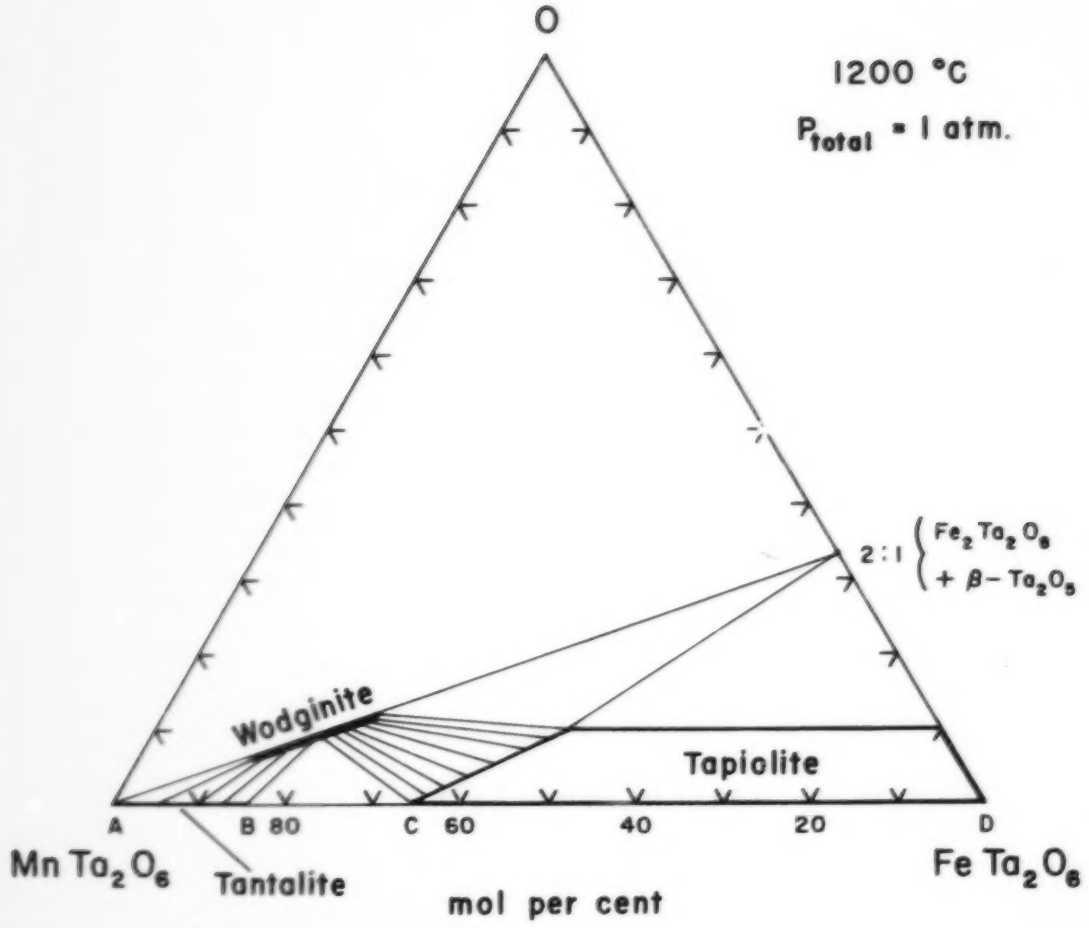

Figure 2. The System $MnTa_2O_6$-$FeTa_2O_6$-O by projection. The phases Wodginite, $Fe_2Ta_2O_8$, β-Ta_2O_5 and the ternary solid solution of tapiolite do not plot exactly on this ternary join, and are therefore shown in projection.

substitution:

$$Fe_2Ta_4O_{12} \longleftrightarrow Fe_3Ta_3O_{12}$$

Complete oxidation of the iron in materials containing both iron and manganese produced the compounds wodginite and (Fe, Mn) TaO_4. The latter compound has a rutile structure. Both coexisted with small amounts of Ta_2O_5, and had bulk compositions in which the weight gain corresponded to the oxygen required to oxidize the iron only. The composition of wodginite was therefore thought to lie on the join $MnTa_2O_6$ - $FeTaO_4$.

THE SYSTEM $Mn_2Ta_4O_{12}$ - $Fe_3Ta_3O_{12}$

The results of syntheses along this join, shown in Figure 3 at the left hand side of the triangle, included wodginite without other phases. The composition of wodginite is therefore:

$Mn^{+2}_{2-2w}\ Fe^{+3}_{3w}\ Ta_{4-w}O_{12}$, with $0.08 < w < 0.23$ at 1200°C. It contains only bivalent manganese and trivalent iron. Other elements found in natural materials, such as tin, are not essential for its formation.

Figure 3 shows a triangular join of 3 solid phases, wodginite + tantalite + tapiolite, which may coexist at univariant equilibrium. All three minerals were identified in the Bernic Lake pegmatite (Nickel et al, 1963), but only wodginite and tapiolite were in close association. This assemblage is at least bivariant; it could be produced either in equilibrium with an intermediate partial pressure of oxygen, or by incomplete reaction of manganese-bearing tapiolite being oxidized to wodginite, or the reverse reduction reaction.

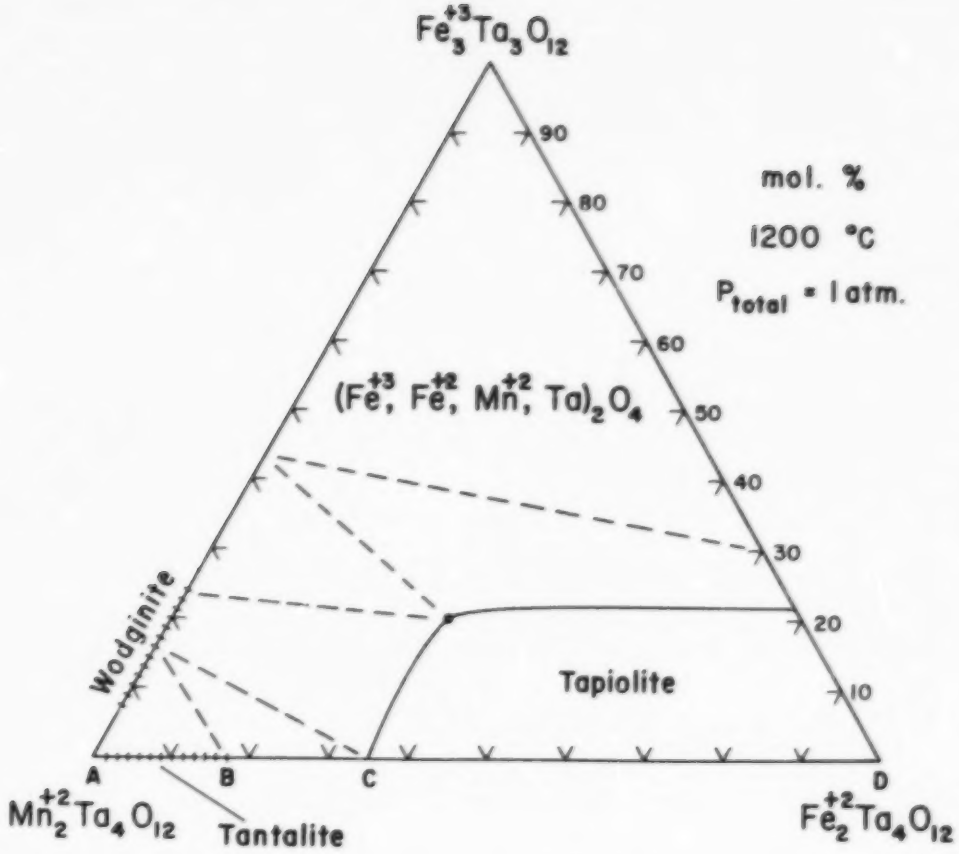

Figure 3. The system $Fe_3Ta_3O_{12}$-$Mn_2Ta_4O_{12}$-$Fe_2Ta_4O_{12}$ at 1200°C, total pressure 1 atm. Field boundaries in the ternary are drawn by extrapolation from the sides, plus projection from the system $MnTa_2O_6$-$FeTa_2O_6$-O for the tapiolite field.

The formation of wodginite requires two conditions:

(1) an oxygen partial pressure greater than that of gas with $CO:CO_2 = 1:10$, and (2) a chemical composition enriched in Mn, Ta and Fe. Such a chemical environment will produce tantalite and tapiolite at lower oxygen pressures. Therefore, wodginite is an indicator of oxidizing conditions during the formation of pegmatites in which it occurs.

ACKNOWLEDGEMENTS

Mr. J.F. Rowland contributed many valuable suggestions.

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